

UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of : **Confirmation No. 8121**

Kazuyuki NITTA et al. : Docket No. 2001-1143A

Serial No. 09/928,430 : Group Art Unit 1752

Filed August 14, 2001 : Examiner S. Lee

POSITIVE-WORKING PHOTORESIST  
COMPOSITION AND RESIST  
PATTERNING METHOD USING SAME

**DECLARATION**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, the undersigned Kazuyuki NITTA, do hereby declare:

THAT I am an employee of Tokyo Ohka Kogyo Co., Ltd., Japan, the assignee of the above-identified United States patent application, since April, 1990, being engaged in the research and development works relative to the chemical-amplification positive-working photoresist compositions and other related products of the company;

THAT, I am one of the joint inventors in the above-identified pending United States patent application, I have full acquaintance with the subject matter of the above-identified pending application and have caused the comparative experiments described below either by myself or under my direct supervision; and

THAT I have a good knowledge of the English language and have read and understood the application papers and the prosecution history of the application.

## COMPARATIVE EXPERIMENTS

### I. Object of experiments

The comparative experiments below describe the results of the experiments conducted with an object to demonstrate the unexpectedly distinctive results obtained with the photoresist composition according to claim 1 after the separately proposed amendment, in which the polyvinyl ether compound as the component (C) is limited to an alicyclic polyvinyl ether compound such as 1,4-cyclohexanedimethanol divinyl ether, as compared with a similar photoresist composition but formulated with a linear aliphatic polyvinyl ether compound as the component (C).

### II. Experimental procedures and results

#### Experiment 1 (inventive).

A positive-working photoresist composition was prepared by uniformly dissolving, in 670 parts by weight of propyleneglycol monomethyl ether, 75 parts by weight of a first polyhydroxystyrene resin having a weight-average molecular weight of 10000 with a molecular weight dispersion of 1.2, of which 39% of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups, 25 parts by weight of a second polyhydroxystyrene resin having a weight-average molecular weight of 10000 with a molecular weight dispersion of 1.2, of which 36% of the hydroxyl groups were substituted for the hydrogen atoms by *tert*-butoxycarbonyl groups, 5 parts by weight of bis(cyclohexylsulfonyl) diazomethane,

5 parts by weight of 1,4-cyclohexanedimethanol divinyl ether,  
0.14 part by weight of salicylic acid and  
0.1 part by weight of triethylamine  
followed by filtration through a membrane filter of 0.2  $\mu\text{m}$  pore  
diameter.

A semiconductor silicon wafer provided on one surface with  
a 0.12  $\mu\text{m}$  thick anti-reflection coating film of an anti-  
reflection coating agent (SWK-EX2, a product by Tokyo Ohka Kogyo  
Co.) was coated with the photoresist composition obtained above  
by using a spinner followed by heating on a hot plate at 90 °C  
for 90 seconds to form a dried photoresist layer having a  
thickness of 0.49  $\mu\text{m}$ . The photoresist layer was exposed  
pattern-wise to KrF excimer laser beams through a pattern-  
bearing photomask on a minifying projection exposure machine  
(Model NSR-S203B, manufactured by Nikon Co.) in an exposure dose  
increased stepwise in an increment of 1 mJ/cm<sup>2</sup> followed by a  
post-exposure baking treatment at 110 °C for 90 seconds and then  
by a development treatment at 23 °C for 60 seconds with a 2.38%  
aqueous solution of tetramethylammonium hydroxide followed by  
rinse with water for 30 seconds and drying to give a resist  
layer with a contact hole pattern of 0.19  $\mu\text{m}$ .

The critical resolution was examined on the patterned  
resist layer with the contact hole pattern obtained in the above  
to find 0.17  $\mu\text{m}$ .

The patterned resist layer obtained in the above was heated  
at 135 °C to cause thermal flow which was examined for the  
contact hole pattern of 0.19  $\mu\text{m}$  diameter and the flow rate, i.e.  
changes in the pattern size per °C, was measured in nm/°C and  
recorded in three ratings of: A for a rate not exceeding 5  
nm/°C; B for a rate of 5 to 15 nm/°C; and C for a rate exceeding  
15 nm/°C.

The thermal flow rate for the patterned resist layer in  
this experiment was 5.0 nm/°C and thus the thermal flow behavior  
was rated as A. SEM photographs taken of the contact hole  
pattern before and after the thermal flow treatment are attached  
hereto as EXHIBIT.

#### Experiment 2 (comparative)

The experimental procedure was just the same as in Experiment 1 described above excepting for the replacement of 5 parts by weight of 1,4-cyclohexanedimethanol divinyl ether in the formulation of the photoresist composition with the same amount of 1,6-hexanediol divinyl ether.

The critical resolution was examined on the patterned resist layer with the contact hole pattern obtained in the above to find 0.18  $\mu\text{m}$ .

The thermal flow rate for the patterned resist layer in this experiment was 12.4 nm/ $^{\circ}\text{C}$  and thus the thermal flow behavior was rated as B. SEM photographs taken of the contact hole pattern before and after the thermal flow treatment are attached hereto as EXHIBIT.

#### Experiment 3 (comparative)

The experimental procedure was just the same as in Experiment 1 described above excepting for the replacement of 5 parts by weight of 1,4-cyclohexanedimethanol divinyl ether in the formulation of the photoresist composition with the same amount of diethyleneglycol divinyl ether.

The critical resolution was examined on the patterned resist layer with the contact hole pattern obtained in the above to find 0.18  $\mu\text{m}$ .

The thermal flow rate for the patterned resist layer in this experiment could not be obtained since a hole pattern had been closed due to too early thermal flow and thus the thermal flow behavior was rated as C. SEM photographs taken of the contact hole pattern before and after the thermal flow treatment are attached hereto as EXHIBIT.

### III. Conclusion

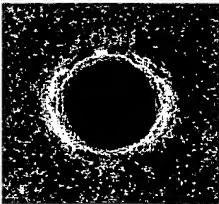
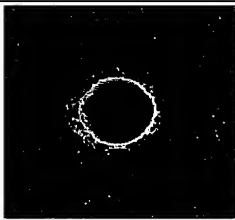
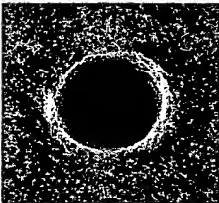
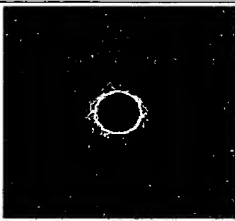
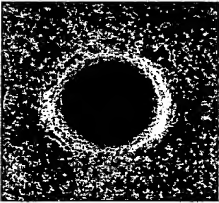
As is clearly understood from comparison of the above-described results of the inventive and comparative experiments, remarkable improvements can be obtained in the thermal flow

behavior as well as the critical pattern resolution by using 1,4-cyclohexanedimethanol divinyl ether as the component (C) in the formulation of the inventive photoresist composition as compared with the photoresist compositions in Experiments 2 and 3 formulated with a linear aliphatic divinyl ether compound.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of any application or any patent issued thereon.

Date: March 29, 2004

Kazuyuki Nitta  
Kazuyuki NITTA

	Before thermal flow treatment	After thermal flow treatment
Experiment 1		
Contact hole diameter	190 nm	140 nm
Experiment 2		
Contact hole diameter	190 nm	66 nm
Experiment 3		No hole pattern
Contact hole diameter	190 nm	

## EXHIBIT

